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Gold(I) and platinum(II) complexes with a new diphosphine ligand based on the cyclotriphosphazene platform

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Experimental

Analytical grade solvents were used as supplied for synthesis with the exception of tetrahydrofuran (THF), which was distilled from sodium/benzophenone. (2-hydroxy-phenyl)diphenylphosphine has been reported previously[1] but was prepared here using a similar procedure for the preparation of (4-hydroxyphenyl)diphenylphosphine.[2] [Au(tht)Cl] (tht = tetrahydrothiophene), 0.05M $AuBF_4$ in CH_3CN and $[M(CO)_4(pip)_2]$ (M = W and Mo, pip = piperidine) and $[N_3P_3(biph)_2Cl_2]$ (biph = 2,2'-biphenol) were prepared according to literature procedures.[3-6] Cyclotriphosphazene ($N_3P_3Cl_6$) was a gift from Otsuka Chemical Company Ltd (Japan) and $Pt(COD)Cl_2$ was obtained from Aldrich. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Brucker Avance 400 spectrometer. Phosphorus chemical shifts are referenced to 85% aqueous H_3PO_4 and proton chemical shifts are referenced to TMS. Electrospray mass spectra were obtained from CH_3CN solutions on a Micromass ZMD spectrometer run in the positive ion mode. Listed peaks correspond to the most abundant isotopomer; assignments were made by a comparison of observed and simulated spectra.

Syntheses

(2-hydroxyphenyl)diphenylphosphine ($HOC_6H_4PPh_2$). A mixture of 2-bromophenol (6 mL, 51.7 mmol), 2-methoxypropane (10 mL, 104.4 mmol) and phosphorus oxychloride (1 drop) was stirred under N_2 for 1 h in the absence of light. NEt_3 (4 drops) was added and the volatiles were removed under vacuum. The residue was dissolved in hexane (55 mL) and to this solution was added dropwise a solution of BuLi (1.7M in hexane, 33.5 mL, 57 mmol). The mixture was stirred for a further 4 h and the white precipitate formed was filtered under N_2 and dried by N_2 flow. The precipitate was dissolved in THF (50 mL) and cooled to -78˚C . To this solution was added dropwise a solution of chlorodiphenylphosphine (7 mL, 39.9 mmol) in THF (50 mL). The yellow solution was allowed to warm to room temperature and stirred over 16 h. A solution of HCl (20%, 25mL) was added and stirred for 3 h. The mixture was extracted with diethyl ether (4 x 40 mL) and the extracts were combined, stirred with Na_2CO_3, filtered, washed with water (3 x 40 mL) and dried over $MgSO_4$. The solvent was removed to give an orange oil that was dissolved in CH_2Cl_2 and passed through a short column of silica gel using CH_2Cl_2 as eluent. Concentration of the eluent on a rotary evaporator yielded a white solid that was filtered, washed with hexane and vacuum dried. Further product was obtained from the filtrate by adding hexane and standing at -4˚C overnight. Yield: 8.0g. ^{1}H NMR ($CDCl_3$): δ 7.38 - 7.24 (m, 11H, aryl), 7.00 – 6.83 (m, 3H, aryl), 6.22 ppm (s, H, OH). ^{31}P{H} NMR ($CDCl_3$): -28.7 ppm (s, P).

$[N_3P_3(biph)_2(OC_6H_4PPh_2)_2]$ (L). To a solution of (2-hydroxyphenyl)diphenylphosphine (0.535g, 1.92 mmol) in THF (70 mL) cooled to 0˚C was added NaH (0.07 g, 60% dispersion in oil washed with hexane, 3 mmol). After stirring for 30 min at room temperature, $[N_3P_3(biph)_2Cl_2]$ (0.5g, 0.87 mmol) was added. The mixture was heated at reflux over 21 h and the solvent removed using a rotary evaporator. The residue was extracted with CH_2Cl_2 (150 mL) and filtered through Celite. The filtrate was taken to dryness using a rotary evaporator, and chromatography on silica using CH_2Cl_2/hexane (1:1) as eluent yielded a pure fraction of the product. Yield: 650 mg. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.0 (d, J_{PP} = 94 Hz, 2P, phosphazene), 9.6 (t, J_{PP} = 95 Hz, P, phosphazene), -15.5 ppm (s, 2P, phosphine). ESMS: 1058 $[MH]^+$. *Anal*. Required for $C_{60}H_{44}N_3O_6P_5$: C, 68.12; H, 4.19; N, 3.97%. Found: C, 68.06; H, 4.48; N, 3.80%.

$[AuL]BF_4 \cdot CH_2Cl_2$ (1). To a solution of L (106 mg, 0.1 mmol) in CH_3CN/CH_2Cl_2 (1:2, *ca.* 20 mL) was added a solution of $AuBF_4$ in CH_3CN (0.05M, 2mL). The solution was stirred at room temperature over 2 h, the volume reduced to *ca.* 4 mL using a stream of N_2 gas and then refrigerated. Slow evaporation of the solution left a crystalline material that was recrystallised from CH_2Cl_2/hexane and dried under vacuum. Yield: 123 mg. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.6 (s, 2P, phosphine), 24.5 (d, J_{PP} = 91 Hz, 2P, phosphazene), 13.2 (t, J_{PP} = 89 Hz, P, phosphazene) ppm. ESMS: 1254 $[AuL]^+$. *Anal*. Required for $C_{61}H_{46}AuBCl_2F_4N_3O_6P_5$: C, 51.36; H, 3.25; N, 2.95%. Found: C, 51.05; H, 3.34; N, 3.28%. X-ray quality crystals of **1**·CH_3CN were grown by vapour diffusion of Et_2O into a CH_3CN solution of the complex.

[{AuCl}$_2$L]·1.5CHCl$_3$ (2). Pentane was allowed to vapour diffuse into a chloroform solution containing [Au(tht)Cl] (31.6 mg, 0.1 mmol) and L (53mg, 0.05 mmol). After 5 days, the crop of white crystals so obtained was filtered, washed with pentane and dried under vacuum. Yield: 64 mg. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.5 (s, 2P, phosphine), 24.0 (d, J_{PP} = 102 Hz, 2P, phosphazene), 6.8 (t, J_{PP} = 102 Hz, P, phosphazene) ppm. ESMS: 1254 $[AuL]^+$. Required for $C_{61.5}H_{45.5}Au_2Cl_{6.75}N_3O_6P_5$: C, 44.62; H, 2.76; N, 2.56%. Found: C, 43.46; H, 2.77; N, 2.45%. Crystals of **2**·2.7$CHCl_3$ suitable for x-ray analysis were obtained by an identical procedure using $[NBu_4][AuCl_2]$ instead of [Au(tht)Cl].

[PtLCl$_2$] (3). A solution of L (0.1g) and $Pt(COD)Cl_2$ (0.035g) in CH_2Cl_2 (20 mL) was heated at reflux over 3.5 h. The solution was concentrated on a rotary evaporator and hexane was added to produce a white precipitate that was collected by filtration, washed with Et_2O and air dried. Yield 100 mg. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.0 - 25.5 (m, 2P, phosphazene), 5.7 - 4.5 (m, P, phosphazene), 7.15 (bs, phosphine, J_{PtP} = 3780 Hz). *Anal.* Required for $C_{60}H_{44}Cl_2N_3O_6P_5Pt$: C, 54.43; H, 3.35; N, 3.17%. Found: C, 54.17; H, 3.37; N, 3.20%. Crystals of **3**·4CH_3CN suitable for x-ray analysis were grown from an acetonitrile solution of the complex.

[W(CO)$_4$L] (4). *cis*-$[W(CO)_4(pip)_2]$ (46.6 mg, 0.1mmol) and **L** (106 mg, 0.1mmol) were combined in toluene (25 mL) and heated at reflux under N_2 for 2 h. The resulting brown solution was filtered and the filtrate was removed on a rotary evaporator to give a brown oil. The product was isolated using column chromatography on silica, eluting with CH_2Cl_2/hexane (1:1). Fractions were combined and concentrated on a rotary evaporator,

initiating crystallisation of the yellow product that was washed with pentane and dried under vacuum. Yield 31 mg. *Anal.* Required for $C_{64}H_{44}N_3O_{10}P_5W$: C, 56.78; H, 3.28; N, 3.10%. Found: C, 57.03; H, 3.51; N, 3.25%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.5 (d, J_{PP} = Hz, 2P, phosphazene), 14.2 (t, J_{WP} = 289 Hz, 2P, phosphine), 3.9 (t, J_{PP} = Hz, P, phosphazene) ppm. ν(CO) cm^{-1}: 2020m, 1918s, 1892s, 1866s.

[Mo (CO)$_4$L] (**5**). *cis*-[$Mo(CO)_4(pip)_2$] (37.8 mg, 0.1 mmol) and L (106 mg, 0.1 mmol) were combined in CH_2Cl_2 (25 mL) and heated at reflux under N_2 over 2 h. The complex was isolated in an analogous manner to [$W(CO)_4$L] (above). Yield 46 mg. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.6 (s, 2P, phosphine), 26.4 (d, J_{PP} = Hz, 2P, phosphazene), 4.1 (t, J_{PP} = Hz, P, phosphazene) ppm. *Anal.* Required for $C_{64}H_{44}MoN_3O_{10}P_5$: C, 60.72; H, 3.50; N, 3.32%. Found: C, 60.77; H, 3.86; N, 3.31%. ν(CO) cm^{-1}: 2023m, 1932s, 1900s, 1868s.

X-ray Crystallography

The x-ray data was collected on a Siemens P4 four circle diffractometer, using a Siemens SMART 1K CCD area detector. The crystals were mounted in an inert oil, transferred into the cold gas stream of the detector and irradiated with graphite monochromated Mo-K_α (λ = 0.71073 Å) x-rays. The data were collected by the SMART program and processed with SAINT to apply Lorentz and polarisation corrections to the diffraction spots (integrated 3 dimensionally). The structures were solved by direct methods and refined using the SHELXTL program. Hydrogen atoms were calculated at ideal positions. For the solution of **2**·2.7$CHCl_3$, the electron density of disordered $CHCl_3$ was

removed from the unit cell using PLATON / SQUEEZE. Approximately 2.7 molecules of $CHCl_3$ per cell were removed (314 e^- per cell and 869 $Å^3$ was left by the void).

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